

Physical Limit of Stability in Supercooled Liquids¹

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ABSTRACT

The kinetic spinodal (KS) in supercooled liquids, similar to the KS in superheated and stretched liquids [*Physica A*, **269**: 252 (1999)], was introduced as a locus where the mean time of formation of a critical nucleus becomes shorter than a relaxation time to local equilibrium. If the surface tension of the solid-liquid interface is known, the kinetic spinodal is completely determined by the equation of state of supercooled liquid. The theory was tested against experimental data on the surface tension and homogeneous nucleation limit for supercooled water. Reasonably good agreement between theoretical predictions and experimental data was achieved. A prediction of the high-temperature limit for glass transitions is also discussed.

KEY WORDS: glass transition; homogeneous nucleation; kinetic spinodal; supercooled water, surface tension.

1. INTRODUCTION

In the usual thermodynamic theory of phase transitions, the spinodal, the locus of states of infinite compressibility, is considered as a boundary of the metastable states in fluids [1]. However, physically the metastable state becomes short-lived well before the spinodal is reached [2, 3]. According to the classical theory of homogeneous nucleation, the life time of the metastable state is determined by the mean time of formation of a critical nucleus of stable phase t_M , which depends on both the thermodynamic and transport properties of fluid (for a review see Ref. [4]). In this theory, a metastable phase is considered a short-lived, but still thermodynamic, state of metastable fluid. In the kinetic theory of relaxation of metastable state developed by Patashinskii and Shumilo [5, 6], the physical boundary of metastable states was introduced as a locus where the mean time of formation of a critical nucleus of stable phase, t_M , becomes shorter than a characteristic time governing the decay of fluctuations to local equilibrium, t_R . When $t_M \leq t_R$, the entire concept of a homogeneous state ceases to be valid, and, as a result of fluctuations, the initial homogeneous state transforms to a heterogeneous state during the time $t \approx t_R$ [6]. The both times, t_M and t_R , depend on the kinetic properties of liquid, but the ratio t_M/t_R depends on the thermodynamic properties only. Therefore, the physical boundary of metastable state, or kinetic spinodal, in this approach is completely determined by the equation of state and by the surface tension.

In the present work, we continue the study of the kinetic boundary of metastable states in fluids initiated in our previous works for vapor-liquid equilibrium [7, 8]. Here we extend this approach to solid-liquid equilibrium and consider the kinetic boundary of

metastable states in supercooled liquids. The theory was tested against experimental data for supercooled water.

2. THEORETICAL BACKGROUND

The dynamics of a system in the metastable state of the initial phase is connected with the relaxation and fluctuations of the hydrodynamic fields of the order parameter $\varphi(\vec{x}, t)$, energy density $\varepsilon(\vec{x}, t)$, etc. [5, 6]. The slowness of their relaxation allows us to exclude other degrees of freedom that supposedly reach local equilibrium. In liquids, we may consider the situation where the dynamics of a single hydrodynamic mode, which is a scalar field of the order parameter only. In this case, the equation of motion of the system is [9]

$$\frac{\partial \varphi}{\partial t} = -\Gamma_c \Delta \left(\frac{\partial H}{\partial \varphi} + f_{st} \right) \quad (1)$$

where Γ_c is a transport coefficient, H is an effective Hamiltonian, and f_{st} is an external random force modeling the thermal fluctuations. The effective Hamiltonian $H\{\varphi\}$ can be expanded in a functional series as in a second-order phase transition. In the vicinity of the stability region, the effective Hamiltonian can be represented in the form [6]

$$H\{\varphi\} = \int d^3r \left(\frac{g}{2} (\nabla \varphi)^2 + \frac{u_2}{2} \varphi^2 + \frac{u_3}{3} \varphi^3 \right), \quad (2)$$

where $g, u_2, u_3 > 0$, and u_2 are assumed to be small. The curve $u_2=0$ represents a bare or “unrenormalized” spinodal (i.e., a spinodal of the system in the absence of fluctuations). The solution of Eqs. (1) and (2), which was obtained by Patashinskii and Shumilo [5, 6], yields a lifetime of the metastable phase, which accounts for fluctuations and is given by equation

$$t_M = t_R \left(\frac{4\pi\gamma}{\lambda_0} \right) \exp(\gamma W_{\min} / kT) \quad (3)$$

where $t_R = 16g / \Gamma_0 u_2^2$ is a characteristic time governing the relaxation toward local equilibrium, W_{\min} is the nucleation barrier, which is equal to the minimum reversible work required to form a critical size nuclear, the dimensionless parameter $\gamma = (u_2 g)^{3/2} / k_B T u_3^2$, and $\lambda_0 \cong 8.25$ is a dimensionless constant. It follows from Eq. (3) that when $\gamma W_{\min} \gg k_B T$ the lifetime of the metastable phase is much longer than the relaxation time t_R . For $\gamma < k_B T / W_{\min}$, the initial homogeneous state that is stable with respect to long-wavelength fluctuations transforms to a heterogeneous state as a result of fluctuations during a time comparable with the time governing the relaxation toward local equilibrium ($t_M \cong t_R$). The curve $\gamma W_{\min} = k_B T$, or, alternatively,

$$u_2 = (u_2)_{KS} = \frac{1}{g} \left[\frac{(k_B T u_3)^2}{W_{\min}} \right]^{2/3}, \quad (4)$$

can be regarded as the physical (kinetic) spinodal, which limits the region in the phase diagram ($u_2 > (u_2)_{KS}$) of statistically well defined and experimentally attainable metastable states. For $0 < u_2 < (u_2)_{KS}$ the lifetime $t_M < t_R$ and the very concept of an equilibrium homogeneous state is no longer applicable, and this spinodal region separates metastable and unstable states in the phase diagram of one-component fluids.

In order to use the theoretical result contained in Eq. (4) for practical calculations of the kinetic boundary of metastable states, we need to know how the parameters u_2 , u_3 , and g of the effective Hamiltonion in Eq. (2) are related to the thermodynamic parameters of the real physical system. As was shown in our previous works [7, 8], parameters u_2

and u_3 are directly related to the first and second derivatives of the chemical potential, μ , with respect to the density

$$u_2 = \rho^2 \left(\frac{\partial \mu}{\partial \rho} \right)_T = k_B T \rho \bar{\mu}_\rho, \quad u_3 = \frac{1}{2} \rho^3 \left(\frac{\partial^2 \mu}{\partial \rho^2} \right)_T = \frac{1}{2} k_B T \rho \bar{\mu}_{\rho\rho} \quad (5)$$

and for the parameter g a good estimate is

$$g = k_B T (\rho^*)^{\frac{1}{3}} \quad (6)$$

where ρ^* is a characteristic density in the system. In the superheated and stretched liquids as a characteristic density in Eq. (6) we used the critical density ρ_c [7, 8], while in supercooled liquids one can set ρ^* equal to the density of liquid in the triple point, $\rho^* = \rho_{tr}$.

Finally, Eq. (4) for the kinetic spinodal T_{KS} in the supercooled liquids with account of Eqs. (5) and (6) can be written in the form

$$\bar{\mu}_\rho(T_{KS}) = \left[\frac{k_B T \bar{\mu}_{\rho\rho}^2(T_{KS})}{4W_{\min}(T_{KS})} \right]^{\frac{2}{3}} \left(\frac{\rho}{\rho_{tr}} \right)^{\frac{1}{3}} \quad (7)$$

where the nucleation barrier for the spherical crystal nuclear in supercooled liquid is given by [2, 3]

$$W_{\min} = \frac{16\pi}{3} \frac{T_m^2(P) \sigma_{SL}^3(T) v_s^2(T)}{\Delta h^2 \Delta T^2} \quad (8)$$

where σ_{SL} is the surface tension at the liquid-crystal interface, v_s is the molar volume of the crystal, Δh is the molar enthalpy of fusion, T_m is a melting temperature at given pressure P , and $\Delta T = T_m - T$ is a degree of supercooling.

3. COMPARISON WITH EXPERIMENTAL DATA

In order to calculate the kinetic boundary of metastable state with Eq. (7), one needs to know the equation of state, which can be extrapolated into the metastable region, and the surface tension. For the vapor-liquid equilibrium such equation of state and the surface tension are usually well known, and the kinetic spinodal in superheated and stretched liquids can be predicted with a high accuracy [7, 8]. In supercooled liquids, the situation is more complicated. The equation of state obtained from the analysis of the experimental data in stable liquid, as a rule, can not be extrapolated into the supercooled region and the solid-liquid surface tension is scarcely known. Unlike the vapor-liquid surface tension, the solid-liquid surface tension can not be measured directly and it is usually determined from the analysis of the experimental data on the nucleation rate in supercooled liquid [2]. It is clear, that the numerical value of the surface tension obtained by this way depends strongly on the theoretical model applied for this analysis. All this increases the uncertainties in the prediction of the kinetic boundary of the metastable state in supercooled liquids.

For a comparison of the theory with experimental data, we consider here the thermodynamic properties of supercooled water. For supercooled water, most of the information about the surface tension was obtained at atmospheric pressure; therefore, we first consider here the isothermal compressibility, K_T , and homogeneous nucleation temperature, T_H , data obtained at $P = 0.1$ MPa by Speedy and Angell [10]. The surface tension σ_{SL} was obtained from a solution of Eq. (7) for the kinetic spinodal where we set $T_{KS} = T_H$, with $T_H = 235.16$ K as obtained by Speedy and Angell [10]. For the representation of the thermodynamic properties of water the IAPWS-95 Formulation [11]

is recommended as a most accurate one. As was pointed up in the IAPWS release [11], this formulation behaves reasonably when extrapolated into the metastable region and represents the available experimental data of supercooled water to within the experimental accuracy. However, it is not clear how this EOS does represent the second derivatives of the pressure respect to density in supercooled water at temperatures close to T_s . Therefore, in order to avoid a misinterpretation of experimental data, the density of liquid and the second derivative $\bar{\mu}_{\rho\rho}$ in Eq. (7) were calculated with the IAPWS-95 Formulation [11] at the melting temperature T_m . Since at low pressures near the melting curve ρ and $\bar{\mu}_{\rho\rho}$ are the slowly varying quantities, we assume this is a reasonable approximation. We calculate the first derivative $\bar{\mu}_\rho(T) = K_T^{-1} / \rho RT$ with the empirical expression for the isothermal compressibility

$$K_T = A_\kappa (T / T_s - 1)^{-\gamma_\kappa} \quad (9)$$

with the parameters $A_\kappa = 296.5 \times 10^{-6}$ MPa, $\gamma_\kappa = 0.349$, and $T_s = 228$ K obtained by Speedy and Angell [10] from a fit of Eq. (9) to their experimental data in supercooled water at $P = 1$ MPa. The melting temperature T_m was calculated with the international equation developed by Wagner *et al.* [12], while for the calculation of the ice density, ρ_s , and heat of fusion, Δh , we used the vapor pressure formulation for ice developed by Wexler [13].

The result of our calculations in comparison with the values of surface tension obtained by other authors is shown in Fig. 1. Our value of surface tension lies between the values $\sigma_{SL} = 0.0287$ J·m⁻² and $\sigma_{SL} = 0.0240$ J·m⁻² obtained at the same temperature by Butorin and Skripov [14] and by Wood and Walton [15], respectively. The surface

tension reported in Refs. [14, 15] was obtained from the analysis of the nucleation rate data and, and, as was pointed out by Butorin and Skripov [14], the difference between them is due to introducing by Wood and Walton [15] an additional temperature-dependent factor $(T_m/T)^2$ into the equation for the nucleation barrier, Eq. (8) . Our value of surface tension, $\sigma_{SL} = 0.0258 \text{ J}\cdot\text{m}^{-2}$, was obtained from a different theoretical model. Therefore, the difference of about $\pm 8\%$ obtained for σ_{SL} in our case can be considered as a reasonably small in view of the uncertainty of nucleation theory. Huang and Bartell [16] for example, obtained the same difference using slightly different modifications of kinetic theory for the analysis of their nucleation rate experimental data at $T = 200 \text{ K}$. At lower temperatures this difference can even increase. A power-law interpolation

$$\sigma(T) = \sigma(T_1)(T/T_1)^{0.3} \quad (10)$$

proposed by Huang and Bartell [16] is also shown in Fig. 1. At $T=235 \text{ K}$, the power-law interpolation gives $\sigma_{SL} = 0.0228 \text{ J}\cdot\text{m}^{-2}$, what is about 5% lower than the value obtained by Wood and Walton [15]. While at low temperatures, $T < 200 \text{ K}$, the values of surface tension calculated with this interpolation lie of about 20-40% higher than ones obtained from the simple linear interpolation

$$\sigma(T) = \sigma(T_1) + (d\sigma/dT)_{T_1}(T - T_1) \quad (11)$$

with $(d\sigma/dT)_{T=-36.55^\circ\text{C}} = 0.211 \times 10^{-2} \text{ J}\cdot\text{m}^{-2}$ obtained by Wood and Walton [15].

In order to estimate the values of the surface tension on other temperatures, we applied the described above procedure to isothermal compressibility and homogeneous nucleation data obtained by Kanno and Angell [17] at higher pressures up to 190 MPa. Filled circles in Fig. 1 show the values of the surface tension obtained by this way. One

can see that despite of expectation the surface tension extracted from our theory in this case is increased with decreasing of temperature. Such behavior of the surface tension is specific for heterogeneous nucleation that can be observed in large volumes [14], rather than for homogeneous nucleation in the small droplets. In Fig. 2, we show the critical radius of the nuclear

$$r_c = \frac{2T_m(P)\sigma_{SL}(T)v_s(T)}{\Delta h\Delta T} \quad (12)$$

calculated with different models for the surface tension at the homogeneous nucleation temperatures reported by Kanno and Angell [17]. At low temperatures, $T < 200$ K, the critical radius of the nuclear calculated with Eqs. (10) and (11), $r_c \approx 0.3\text{-}0.9$ nm, becomes comparable with the characteristic size of the network defects in liquid water [18]. In principle, in this case the network defects can play a role of the nucleation centers and can stimulate the heterogeneous nucleation even in the small droplets. Although there are also some other indications that liquid water can exist down to $T=150$ K [19], we have no solid evidence that data reported by Kanno and Angell [17] correspond to heterogeneous nucleation. Therefore, we assume here that this unusual temperature behavior of the surface tension is a result of extrapolation of the quantity $\bar{\mu}_{\rho\rho}$ obtained at the melting temperature to the homogeneous nucleation temperature T_H at these pressures. In order to correct this behavior of the surface tension at low temperatures we, on the second step, used at all pressures the value $\bar{\mu}_{\rho\rho} = 74.1$ obtained at $P=0.1$ MPa. The results for the surface tension obtained with this constant value of the parameter $\bar{\mu}_{\rho\rho}$ are shown in Fig. 1 by empty circles. In this case, in the entire temperature range $180\text{ K} < T < T_m$ the surface tension can be treated as a temperature independent constant,

$\sigma_{SL} = 0.0270 \pm 0.0012 \text{ J}\cdot\text{m}^{-2}$. This value is about of 20% bigger than the values obtained from the power-law interpolation of Huang and Bartell [16] and about of 20% smaller than values calculated from the Turnbull's expression [20]

$$\sigma_{SL} = \alpha \frac{\Delta h}{v_s^{2/3}} \quad (13)$$

with $\alpha = 0.32$ originally recommended for water by Turnbull [20].

In Fig. 3, we show the temperatures at the kinetic spinodal, T_{KS} , calculated from Eq. (7) with the surface tension $\sigma_{SL} = 0.0270 \text{ J}\cdot\text{m}^{-2}$ and with the surface tension calculated with Eq. (13). In both cases, T_{KS} satisfies to the obvious condition $T_S < T_{KS} \leq T_H$, or equivalently $(u_2)_S < (u_2)_{KS} < (u_2)_H$. Since the kinetic spinodal represents the boundary behind which no equilibrium thermodynamic state can exist, we consider here the lowest temperatures (i.e., T_{KS} calculated with the surface tension as given by Eq. (13)) as a physical boundary of metastable states in supercooled water. The shaded area in Fig. 3 marks the region where no thermodynamic state for liquid water is possible. This is a “non-thermodynamic habitat” for liquid water not because in this region the parameter $\bar{\mu}_\rho < 0$, which violates the thermodynamic condition of mechanical stability. The first derivative $\bar{\mu}_\rho$, or equivalently the parameter u_2 in Eq. (2), can remain small but positive in this region. It is a “non-thermodynamic habitat” because the lifetime of the homogeneous state in this region is smaller than the time to establish local equilibrium. Therefore, any equilibrium homogeneous state for liquid water is not possible in this region.

4. DISCUSSION

In the present work, we developed a general approach to predicting of the physical boundary of metastable states – kinetic spinodal in supercooled liquids. This approach requires only the equation of state and solid-liquid surface tension for the accurate prediction of the kinetic spinodal in supercooled liquids. The approach can be applied to any supercooled liquid with the scalar order parameter, including liquid metals. Here we applied this method for the calculation of the surface tension and the kinetic spinodal in supercooled water. A reasonably good agreement between experimental data was achieved.

Although water is the most common and best studied liquid, the peculiar behavior of its physical properties in supercooled regime is still a puzzle for investigators [21], and it remains the most difficult fluid to modeling. Only during the last four-five years, several different models and equations of state were developed to represent the anomalous behavior of liquid water in the supercooled regime [22-29]. Our approach can not solve the problem of the describing the thermodynamic properties of supercooled water. However, it can be used as a test on the thermodynamic consistency of the already developed models, as it was done in superheated and stretched water [30].

As example, we applied this method to the new analytical (NA) equation of state for supercooled water developed recently by Jeffery and Austin [29]. This equation predicts the existence of the second critical point (CP_2) related to the low density water (LDW) – high density water (HDW) phase equilibrium, and qualitatively reproduces the anomalous behavior of the isothermal compressibility in supercooled water. However, the quantitative difference between experimental and calculated values of the isothermal

compressibility in supercooled water is significant (see Fig. 4). Because of the positions of the CP₂ ($T_{c2} = 228.3$ K, $P_{c2} = 95.3$ MPa, and $\rho_{c2} = 1042$ kg m⁻³) the maximum compressibility calculated with NA EOS corresponds to the isobar $P = 100$ MPa, but not to $P = 0.1$ MPa, as observed in the experiment. As a consequence, the kinetic spinodal calculated with this equation of state lies above the homogeneous nucleation temperatures, what is physically incorrect. The phase diagram and the kinetic spinodal calculated with this equation are shown in Fig. 5. The principle difference between this diagram and the phase diagram shown in Fig. 3 is that since Eq. (7) now has two roots, T_{KS1} and T_{KS2} , and the “non-thermodynamic habitat” for supercooled liquid water now has a shape of the belt. The second critical point and the LDW-HDW coexistence curve lie inside the “non-thermodynamic habitat” belt, and, therefore, they have no physical meaning. Nevertheless, in principle, the conception of the second – “virtual critical point” can be useful if it yields a good representation of the thermodynamic properties of supercooled water outside the “non-thermodynamic habitat” belt created by this “virtual critical point” itself.

A possible physical interpretation of the second kinetic spinodal temperature T_{KS2} is that this temperature corresponds to the upper temperature limit where the glass transition at a given pressure is possible. For example, at $P = 0.1$ MPa, the temperature T_{KS1} calculated with the NA EOS [29], is about 16 K higher than the homogeneous nucleation temperature obtained by Speedy and Angell [10]. After a shift of the second kinetic spinodal temperature T_{KS2} at the same value, one obtains $T_{KS2}^{shift} = 167$ K, which is a reasonable estimate for the glass transition limit at this pressure. In order to give a more

accurate prediction of the glass transition limit in supercooled liquids, we need both, a better EOS and additional theoretical study of this phenomenon.

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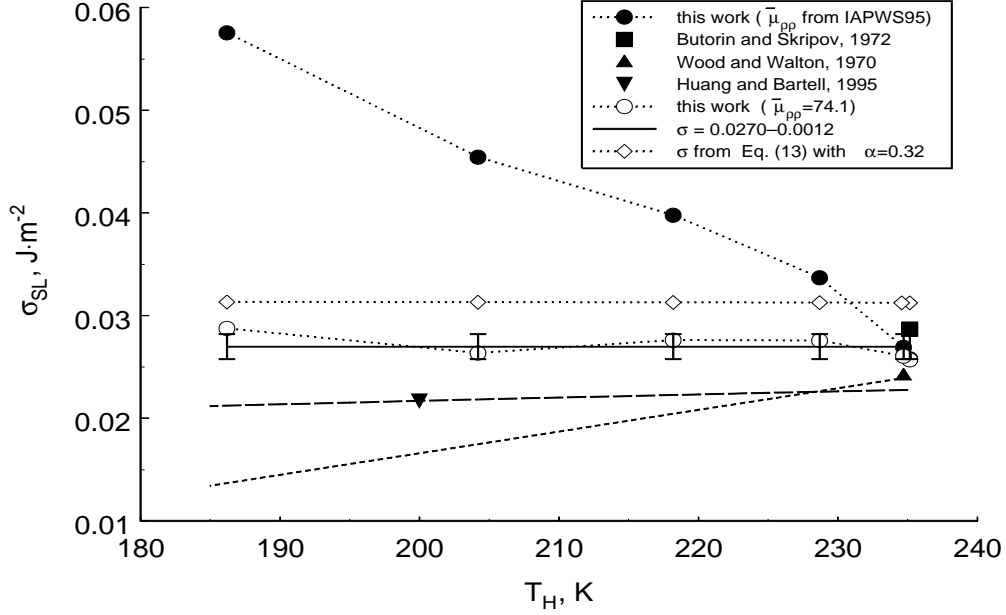


Fig. 1. The ice-water surface tension as a function of temperature. The filled circles with the dotted eye-guide lines represent the values calculated with Eq. (7) with $T_{KS} = T_H$ and $\bar{\mu}_{pp}(T_m)$ obtained from the IAPWS-95 Formulation [11] at different pressures along the melting curve, the open circles correspond to the values calculated with Eq. (7) with $\bar{\mu}_{pp}=74.1$, the open diamonds correspond to the values calculated with Eq. (13) with $\alpha=0.32$. The filled symbols correspond to experimental data obtained by Butorin and Skripov [14] (squares), by Wood and Walton [15] (triangles up), and by Huang and Bartell [16] (triangles down). The solid line corresponds to the constant value $\sigma_{SL} = 0.027 \text{ J}\cdot\text{m}^{-2}$; the long- and short-dashed lines represent the values calculated with Eq. (25) in Ref. [15] and with Eq. (3) in Ref. [16], respectively.

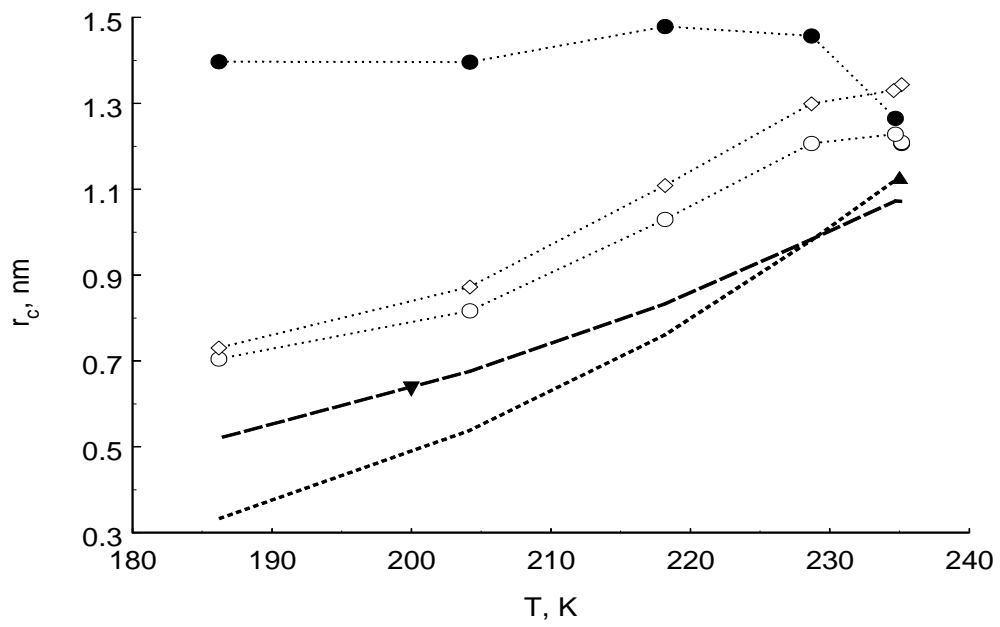


Fig. 2. The critical radius of the nucleus in supercooled water as a function of temperature. The legend as in Fig. 1.

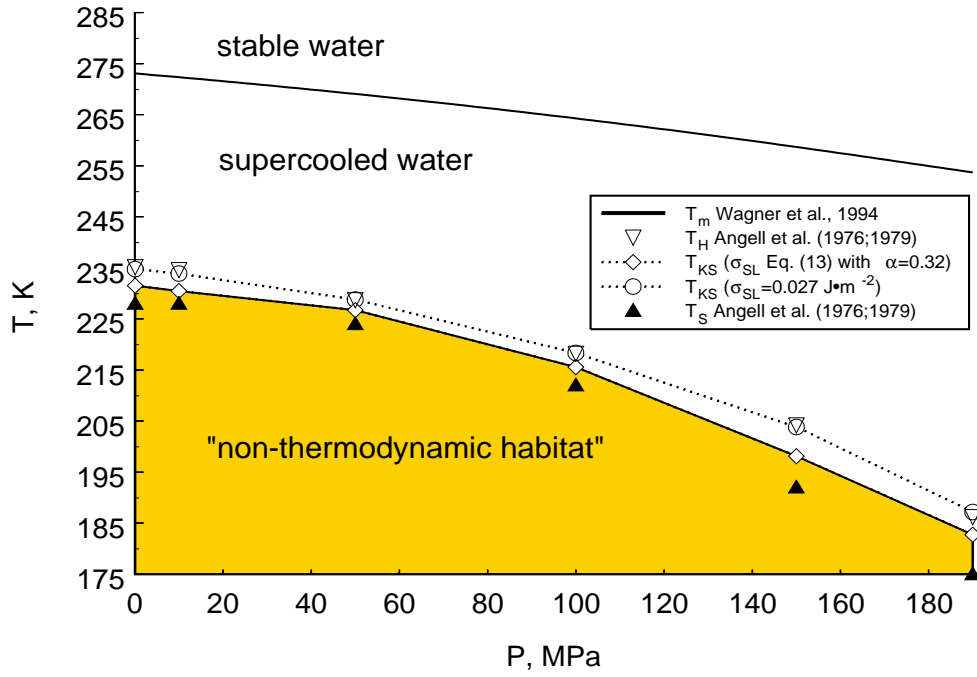


Fig. 3. The phase diagram of supercooled water. The solid line represents the melting curve [12], the open diamonds and circles with the eye-guide lines correspond to the kinetic spinodal temperatures, T_{KS} , calculated with Eq. (7) with different approximations for the surface tension, and the symbols represent the homogeneous nucleation, T_H (triangles down), and spinodal, T_S (triangles up), temperatures obtained by Angell *et al.* [10, 17].

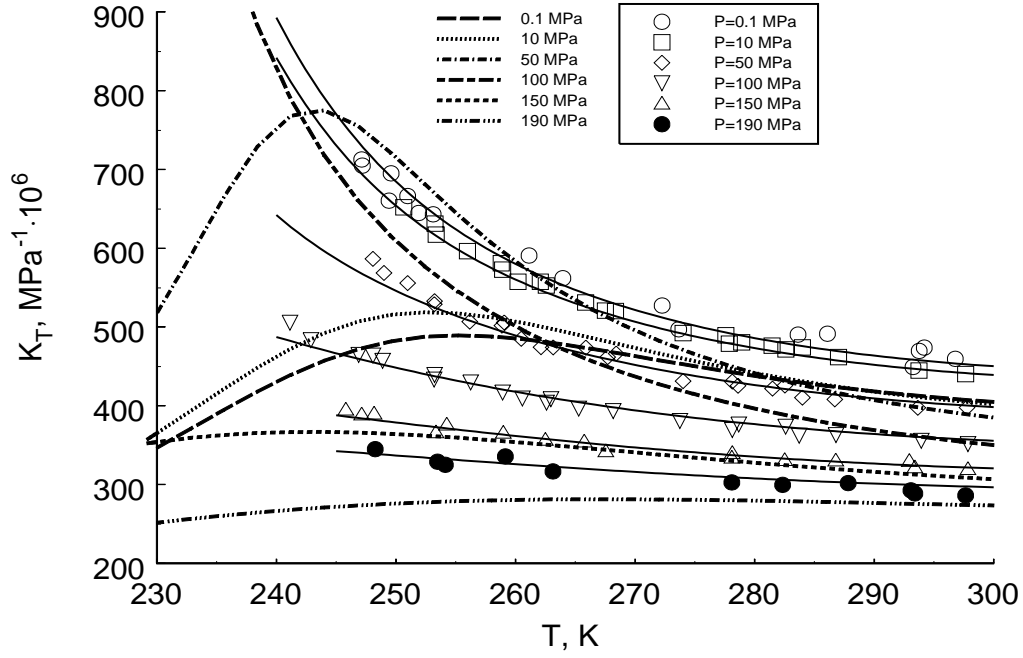


Fig. 4. The isothermal compressibility of water at different pressures in normal and supercooled states as a function of temperature. The symbols represent experimental values obtained by Angell *et al.* [10, 17], the solid curves represent the values calculated with IAPWS-95 Formulation [11], and the dotted-dashed curves correspond to the values calculated with the new analytic equation of state of Jeffery and Austin [29].

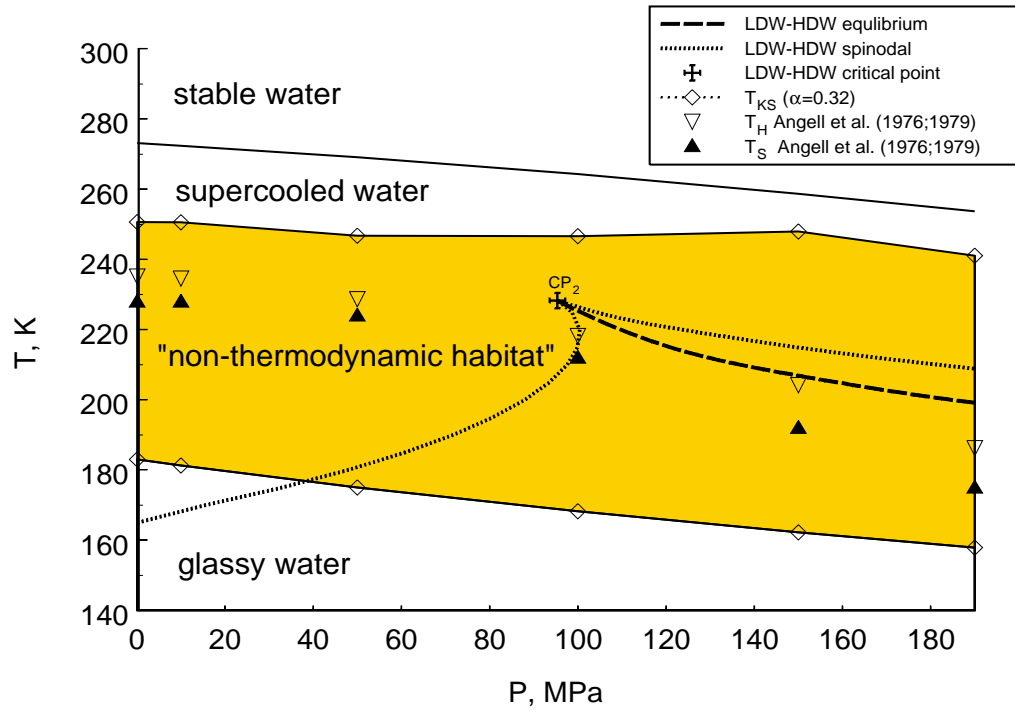


Fig. 5. The phase diagram of supercooled water calculated with the new analytic equation of state of Jeffery and Austin [29]. The cross corresponds to the critical point of LDW-HDW equilibrium (dashed curve), the dotted curves correspond to the LDW-HDW spinodals. The other legend as in Fig. 2.

REFERENCES

1. Landau, L.D. and E.M. Lifshitz, *Statistical Physics, Part 1*. 1980, New York: Pergamon Press.
2. Skripov, V.P., *Metastable Liquids*. 1972, New York: John Wiley & Sons. P.1-272.
3. Debenedetti, P.G., *Metastable Liquids: Concepts and Principles*. 1996, Princeton, NJ: Princeton University Press. 411.
4. Abraham, F.F., *Homogeneous Nucleation Theory*. 1974, New York: Academic Press.
5. Patashinskii, A.Z. and B.I. Shumilo, *Theory of relaxation of metastable states*. Sov. Phys. JETP, 1979. **50**: p. 712-719.
6. Patashinskii, A.Z. and B.I. Shumilo, *Metastable systems near the instability region*. Sov. Phys. Solid State, 1980. **22**: p. 655-659.
7. Kiselev, S.B., J.M.H. Levelt-Sengers, and Q. Zheng, *Physical limit to the stability of superheated and stretched water*, in *Physical Chemistry of Aqueous System: Meeting the Needs of Industry*, H.J. White, J.V. Sengers, D.B. Neumann, and Bellows, J.C., Editor. 1995, Begell House: N.Y.-Wallingford. p. 378-385.
8. Kiselev, S.B., *Kinetic boundary of metastable states in superheated and stretched liquids*. Physica A, 1999. **269**: p. 252-268.
9. Patashinskii, A.Z. and V.L. Pokrovskii, *Fluctuation Theory of Phase Transitions*. 3rd ed. 1979, New York: Pergamon.

10. Speedy, R.J. and C.A. Angell, *Isothermal compressibility of supercooled water and evidence for a thermodynamic singularity at -45 C*. J. Chem. Phys., 1976. **65**(3): p. 851-858.
11. *Release of the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use*. 1996, Frederica, Denmark. Available from the IAPWS Executive Secretary: Dr. R.B. Dooley, Electric Power Research Institute, 3412 Hillview Av., Palo Alto, CA 94304, USA.
12. Wagner, W., A. Saul, and A. Pruss, *International Equations for the Pressure along the Melting and along the Sublimation Curve of Ordinary Water*. J. Phys. Chem. Ref. Data, 1993. **23**(3): p. 515-527.
13. Wexler, A., *Vapor Pressure Formulation for Ice*. J. Res. of NBS, 1976. **81A**(1): p. 5-20.
14. Butorin, G.T. and V.P. Skripov, *Crystallization of Supercooled Water*. Sov. Phys. Crystallography, 1972. **17**(2): p. 322-326.
15. Wood, G.R. and A.G. Walton, *Homogeneous Nucleation Kinetics of Ice from Water*. J. Appl. Phys., 1970. **41**(7): p. 3027-3036.
16. Huang, J. and L.S. Bartell, *Kinetics of Homogeneous Nucleation in the Freezing of Large Water Clusters*. J. Phys. Chem., 1995. **99**(12): p. 3924-3931.
17. Kanno, H. and C.A. Angell, *Water: Anomalous compressibilities to 1.9 kbar and correlation with supercooling limits*. J. Chem. Phys., 1979. **70**(9): p. 4008-4016.
18. Sciortino, F., A. Geiger, and H.E. Stanley, *Network defects and molecular mobility in liquid water*. J. Chem. Phys., 1992. **96**(5): p. 3857-3865.

19. Smith, R.S. and B.D. Kay, *The existence of supercooled water at 150 K*. Nature, 1999. **398**: p. 788-791.
20. Turnbull, D., *Formation of Crystal Nuclear in Liquid Metals*. J. Appl. Phys., 1950. **21**: p. 1022-1028.
21. Stanley, H.E., et al., *The puzzle of liquid water: a very complex fluid*. Physica D, 1999. **133**: p. 453-462.
22. Sastry, S., et al., *Singularity-free interpretation of the thermodynamics of supercooled water*. Phys. Rev. E, 1996. **53**(6): p. 6144-6154.
23. Sciortino, F., et al., *Line of compressibility maxima in the phase diagram of supercooled water*. Phys. Rev. E, 1997. **55**(1): p. 727-737.
24. Rebelo, L.P.N., P.G. Debenedetti, and S. Satry, *Singularity-free interpretation of the thermodynamics of supercooled water II. Thermal and volumetric behavior*. J. Chem. Phys., 1998. **109**(2): p. 626-633.
25. Truskett, M.T., et al., *A single-bond approach to orientation-dependent interactions and its implications for liquid water*. J. Chem. Phys., 1999. **111**(6): p. 2647-2656.
26. Tanaka, H., *Phase behaviors of supercooled water: Reconciling a critical point of amorphous ices with spinodal instability*. J. Chem. Phys., 1996. **105**(12): p. 5099-5111.
27. Bartell, L.S., *On Possible Interpretation of the Anomalous Properties of Supercooled Water*. J. Phys. Chem., 1997. **101**(38): p. 7573-7583.

28. Ponyatovsky, E.G., V.V. Sinityn, and T.A. Pozdnyakova, *The metastable T-P phase diagram and anomalous thermodynamic properties of supercooled water*. J. Chem. Phys., 1998. **109**(6): p. 2413-2422.
29. Jeffery, C.A. and P.H. Austin, *A new analytic equation of state for liquid water*. J. Chem. Phys., 1999. **110**(1): p. 484-496.
30. Kiselev, S.B., et al., *Metastable States of Water and Steam. Part III. Physical Limits of the Stability of water; Implications for formulations*. Report to the IAPWS Meeting, September 30. 1993.